Letters to the Editor

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STUDIES ON PHASE TRANSITION OF SYNTHETIC $\gamma - Fe_2O_3\,H_2O$

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The X-ray powder diffraction study of the structural changes of synthetic γ-Fe_2O_3 . H_2O (lepidocrocite, orthorhombic) due to heat treatment by Williams and Thewlis (1931) appears to show that the substance starts being dehydrated to the ferromagnetic γ-Fe_2O_3 (maghaemite, cubic) at about 250°C. The formation of γ-Fe_2O_3 appears to be complete at 300°C. No further change in crystal structure is observed up to 450°C, but at 500°C lines of α-Fe_2O_3 (haematite, antiferromagnetic, hexagonal) appear in the X-ray powder diagram. Presence of γ-Fe_2O_3 is observable at 550°C, but X-ray photographs of the sample heated to higher temperatures show only lines of α-Fe_2O_3. Later works of Bernal, Dasgupta and Mackay (1957) show that precipitated lepidocrocite begins to lose water at 180°C, and is completely converted into maghaemite and some haematite at 200°C, all maghaemite being converted to haematite below 250°C. A natural crystal of lepidocrocite, according to them, seems to be more stable, and can be heated in air to 235°C without any change. Only at 250°C it is transformed to an oriented texture of a spinel phase and haematite. One half molecule of water begins to come off at about 240°C, and the entire water is lost at about 300°C. The presence of a magnetic phase was observed above 240°C.

Such controversial findings by earlier workers led the anthors to undertake a thorough investigation on the subject. $\gamma - Fe_2O_3.H_2O$ was prepared by precipitation from dilute solution of ferrous chloride with barium hydroxide in the form of suspension in water, and subsequent slow oxidation at room temperature. The carefully washed final precipitate, dried at room temperature, showed the lines of lepidocrocite in the X-ray powder diagram. The dehydration curve of this specimen shows that at about 130°C, the sample starts losing water at a rapid rate which continues upto about 160°C, total loss corresponding to about half a molecule of water. Then the rate of loss decreases, so that there is a kink in the curve at about 160°C, which is also corroborated from the X-ray powder photographs showing lines of maghaemite in this region. Magnetic test indicates that the product obtained above 160°C is ferromagnetic. Loss of water is complete above about 260°C. It is very possible that near about 160°C a distinct phase of the oxide, namely, $Fe_2O_3.\frac{1}{2}\ H_2O$ (turgite) (Mellor, 1934) exists, as indicated by the kink in the dehydration curve, the magnetic behaviour, and certain weak new lines in the diffraction pattern, though the existence of such a hydrate has been denied by some authors. The formation of maghaemite is complete above about 260°C.

The differential thermal curve also gives similar results. There is an endothermal peak extending from about 65°C to 145°C, indicating the removal of adsorbed water. Then there is a flat exothermal peak, extending from about 145°C to about 265°C, which shows the formation of maghaemite through the intermediate phase of turgite A large endothermal peak follows, extending from about 265°C to 370°C, which is however not associated with any structural change as shown by diffraction patterns. This peak may be then due to an order-to-disorder transition of maghaemite associated with the ferromagnetic Curie temperature. Some ferromagnetism, however, still persists upto the middle of the next endothermal peak, extending from 370°C to 475°C, where the transition from maghaemite to haematite seems to be complete as seen from the diffraction pattern. The reason for this is not yet clear.

Detailed investigations comprising of magnetic and X-ray studies are being pursued, and the final results will be published in due course.

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